

Electronic and Geometric Structure of Pu Metal: A High-Resolution Photoelectron Spectromicroscopy Study

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INTRODUCTION

The physical characteristics of any given material are largely derived from the behavior of its valence electrons. Valence electrons are the lowest energy electrons in a material and are responsible for the formation of chemical bonds. Typically, in a metal, electrons are either localized around a particular atom or are delocalized (i.e. shared by all the atoms in the crystal) throughout the entire metal. The actinide series is interesting because as the atomic number increases across the series, the electrons in the actinide metals transition from delocalized 5f electrons (Ac–Pu) to localized 5f electrons (Pu–No). Plutonium (element 94) is located right at this transition. This placement in the series leads to plutonium metal being one of the most complex materials known. Metallic plutonium displays six allotropic phases (α , β , γ , δ , δ' , and ϵ) at standard pressure. A 20% volume expansion occurs during the change from the α phase to the δ phase. These physical properties have been attributed to the 5f valence electrons changing from delocalized states to localized states as the crystal structure changes from the α to the δ phase.

Soft x-ray techniques (photon energy in the range of 10–1000 eV) such as photoelectron; x-ray emission; and near-edge, x-ray absorption spectroscopies have been used to determine the electronic structure of many (in fact most) materials. However, these techniques have not been fully utilized on the actinides. The safety issues involved in handling the actinides make it necessary to minimize the amount of radioactive materials used in the measurements. To our knowledge, the only synchrotron radiation source in the world where soft x-ray measurements have been performed on plutonium is the Spectromicroscopy Facility at Beam Line 7.0.1 at the Advanced Light Source (ALS).

The Spectromicroscopy Facility is designed so that measurements can be made on small quantities of hazardous material. This facility has a photon flux of 10^{13} photon/sec at a photon energy of 100 eV with 0.01 eV resolution. The high photon flux allows one to focus the beam down to a size of 50 microns and still have enough light intensity at the sample for measurements to be conducted in a reasonable time frame 1–10 minutes per spectrum. Therefore, the sample size can be on the order of 100 microns in diameter. This greatly minimizes the amount of plutonium on site during the experiment.

RESULTS

We performed core-level photoemission, valence band photoemission, and near-edge x-ray absorption spectroscopy on both polycrystalline α -plutonium and δ -plutonium microcrystals. Only the photoemission experiments will be described here. Photoelectron spectroscopy is predicated upon the photoelectric effect first described by Einstein in 1905. An incident photon is absorbed by an atom in the solid, and an electron is ejected. An electron energy analyzer is used to measure the direction and kinetic energy of the emitted electron. The kinetic energy of the photoelectron is directly related to its binding energy in the solid.

Figure 1 shows the Pu 4f core-level photoemission spectra from the α - and δ -plutonium samples.

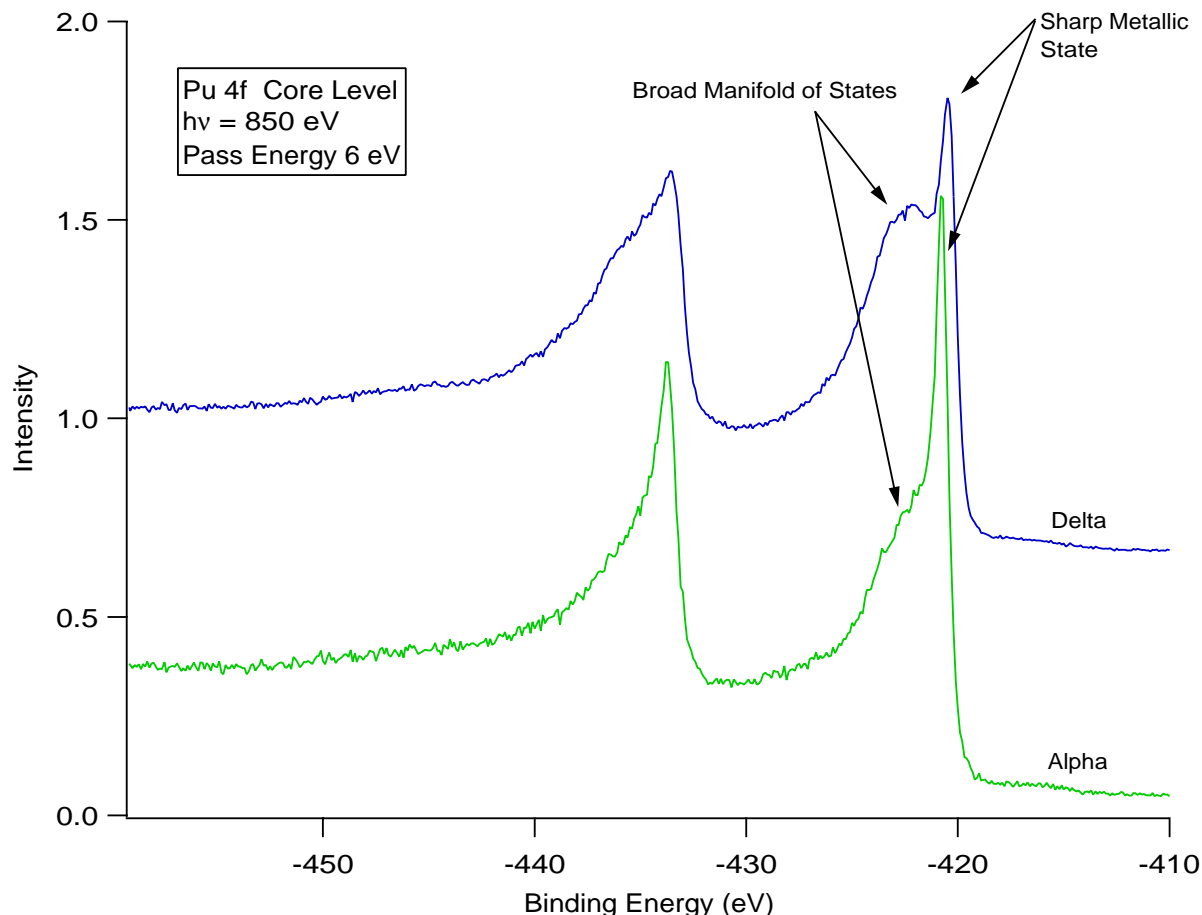


Figure 1: Core-level photoemission spectra from a large crystallite δ -plutonium sample and a polycrystalline α -plutonium sample are shown. These spectra were collected with a photon energy of 850 eV and an analyzer pass energy of 6 eV. Note that two large components are visible in each spectrum, a sharp feature at low binding energy and a broad feature at higher binding energy.

The spectrum arising from core-level photoemission is sensitive to energy differences in the initial state (no core hole) and the final state (core hole and free photoelectron). The two core-level spectra in Figure 1 are similar in that they both show two features, a sharp feature at low binding energy and a broad feature at higher binding energy. The low-binding-energy feature can be ascribed to a metallic initial state with a delocalized final state. As the 5f electrons are more delocalized in the α - than in the δ -plutonium, the greater number of delocalized electrons in the α -plutonium leads to greater intensity in this peak than the δ -plutonium.

Presently, the higher-binding-energy feature is not completely understood. It is likely that this feature has two states contributing to it. We believe that, in simplistic forms, one possible component contributing to the feature is made up of emission to an electronic final state with localized 5f electrons. If this is the case, it suggests that both localized and delocalized 5f electrons are present in the α - and δ -plutonium phases. The second possible component of this feature is from an initial state that has been oxidized.

Valence band spectra show that a small amount of oxygen remains on the surface after the sample preparation. The binding energy of PuO_x is higher than that of the metal and would be expected to

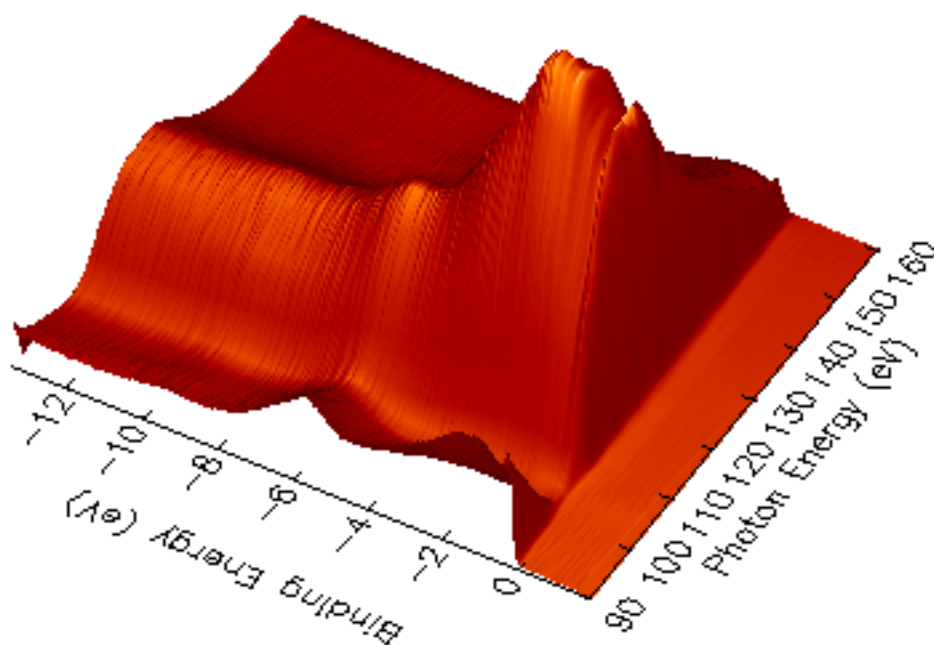


Figure 2(a): The 5d–5f resonant photoemission spectrum with analyzer pass energy of 1 eV showing the 5f density of states in the valence band from a large crystallite δ -plutonium sample.

be seen around the position of the unknown high-binding-energy feature. A final determination of the exact nature of this high-binding-energy feature will shed light on the poorly understood valence electronic structure of plutonium, as well as on the presence of localized and delocalized 5f electrons in the different plutonium phases.

Our initial goal of the valence electronic structure measurements was to determine the density-of-states of the 5f valence electrons in α - and δ -plutonium. This experiment can be directly compared with electronic structure calculations performed by theoreticians. Figures 2(a and b) show the resonant photoemission spectra of the valence band from δ - and α -plutonium, respectively. In a resonant photoemission experiment, valence band photoemission spectra are collected as the photon energy is scanned through a core-level absorption edge. This can result in an enhancement of the emission from specific valence levels. In the case of plutonium, scanning the photon energy through the 5d absorption edge results in a resonant enhancement of the 5f valence emission. The 5d–5f resonant photoemission measurements in plutonium are a measurement of the 5f contribution to the valence density of states.

Two types of information are obtained in the resonant photoemission measurements that can greatly enhance the understanding of plutonium metal. Two-dimensional data slices can be taken in either the constant-photon-energy direction or the constant-binding-energy direction. Slices taken with a constant photon energy are the equivalent to standard photoemission spectra with the exception that specific valence states are emphasized. Different states turn on or become enhanced at different photon energies.

The data in Figures 2(a and b) show clear differences in the resonant photoemission spectra from the α - and δ -plutonium. This is most evident in the state at binding energy 0 eV. If this peak is followed as the photon energy is varied, one notices that in the δ -plutonium (Figure 2a) after 100 eV, the peak smoothly increased to a maximum and then smoothly decreased after the maximum was reached. In direct contrast, the α -plutonium (Figure 2b) showed oscillatory behavior after the ini-

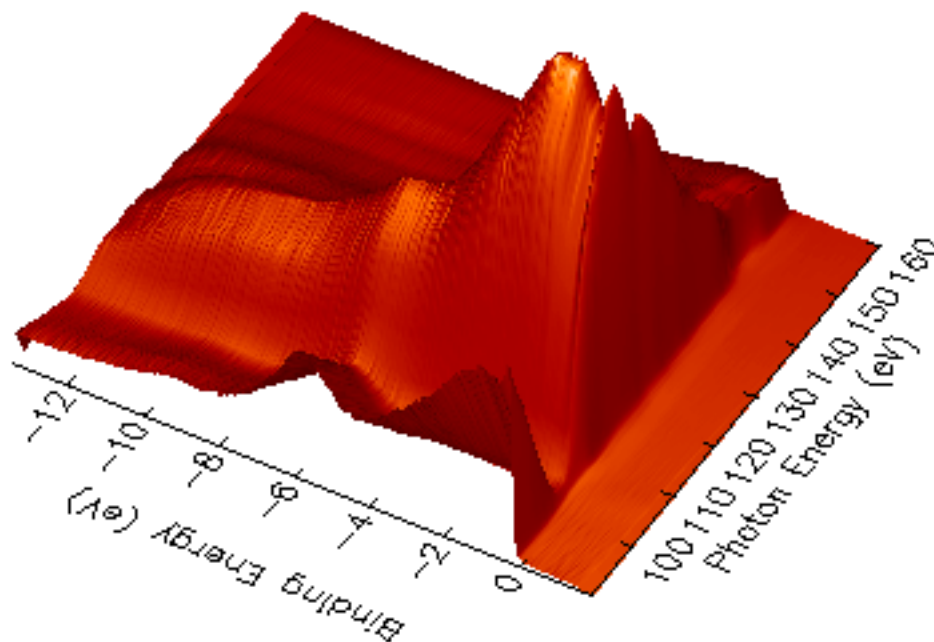


Figure 2(b): The 5d–5f resonant photoemission spectrum with analyzer pass energy of 1 eV showing the 5f density of states in the valence band from a polycrystalline α -plutonium sample.

tial maximum was reached. Theoretical calculations of the resonant photoemission are currently ongoing to try to understand these differences.

A large theoretical effort has been undertaken to understand the plutonium data that we have collected. The next phase of the valence-band, electronic structure measurements will involve measuring the electron dispersion relation (band structure) of the valence electrons in δ -plutonium, and the data will be compared with theoretical calculations. The band structure can only be measured on a single crystal of a material, and it is imperative to have excellent crystals for the measurement. Future investigations will be based upon spin-resolving and photon-dichroic photoelectron spectroscopy. The photon-dichroic measurements include the variant magnetic x-ray linear dichroism.

The unique 5f valence electronic properties of plutonium metal cannot be explained by the typical one-electron calculations used to describe prototypical metals. Calculations on plutonium metal incorporate these properties into calculations in an ad hoc manner. We can measure these effects directly to further our understanding of one of the most complex materials known.

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